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Diffuse phase transition in $Pb_2Bi_3GdTi_5O_{18}$ ceramic

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Abstract : Single phase orthorhombic tungsten bronze ceramics of $Pb_2Bi_3GdTi_5O_{18}$ (PBGT) were prepared by a high temperature solid-state reaction method. Electrical impedance, phase angle, dielectric constant and dielectric loss have been measured in the frequency range 0.1 kHz to 3 MHz in the temperature region 25°C to 300°C. Dielectric studies show PBGT have low dielectric constant, low loss and undergo diffuse phase transition at 226°C. AC impedance analyses suggested the phase element to be capacitive. The activation energy has been estimated to be 0.598eV from the temperature variation of dc conductivity. The nature of variation of conductivity with temperature suggested NTCR behaviour.

Keywords : Phase transition, dielectric constant, ceramic, tungsten-bronze structure.

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1. Introduction

Ferroelectric materials of tungsten-bronze (TB) family have received considerable attention for several years owing to their promising applications in many electronic devices which include integrated non-volatile and dynamic random access memory (DRAM), delay line, pyroelectric detector, piezoelectric and acoustic transducer, microwave resonator, phase shifter, *etc.* [1–5]. The TB-type structure is similar to perovskite structure (ABO_3-type), which consists of a complex array of disordered BO_6 octahederal sharing corners in such a way that three different types of cation sites are available [6,7]. Major stimuli for development of these materials, either in the form of solid solution or dopant additions, have been the prospect of improving their performance characteristics compared to the simple one since they are having highly tolerant structure that allows their electrical properties to be controlled by variable modifications either at A1, A2, C-sites or B1, B2-sites. A number of works on TB materials such as : $(Sr,Ba)Nb_2O_6$ [8,9], $(Pb,Ba)Nb_2O_6$ [10], rare-earth doped $(Sr,Ba)Nb_2O_6$ [11], $Pb_2Bi_4Ti_5O_{18}$ [12], $(Pb,K)LiTa_{10}O_{30}$ [1], $Ba_2NaNB_5O_{15}$ [13], $Ba_2Na_3RNb_{10}O_{30}$ (R = rare-earth ions) [14], $Ba_5RTi_3Nb_7O_{30}$ (R = Dy, Sm) [15], (R = Nd, Eu, Gd) [161, $Ba_4R_2Ti_4Nb_6O_{30}$ (R = Y, Sm, Dy) [17], $Ba_5Nd(Ti,Zr)Nb_7O_{30}$ [18], *etc.* have been reported. It has been observed that compounds of this family undergo phase transition well above and below the room temperature with sharp and/or diffuse type. [6,19]. Further, it is known that the size of substituted ions, chemical composition, microstructure and sintering processes have significant effect on the diffuseness of the phase transition (*i.e.* transition broadening) in this family. The transition broadening is very common occurrence in solid solution and other disordered structures. Therefore, multiple ion occupation cause deviation from Curie-Weiss behaviour, where the ferro-paraelectric phase transition temperature (T_c) is not sharp but physical properties change rather gradually over a temperature range and is known as diffuse phase transition (DPT) [20].

In our earlier work [21], results on $Pb_2Bi_3NdTi_5O_{18}$ have been reported. The present compound $Pb_2Bi_3GdTi_5O_{18}$ is analogous to the above compound. No report, to our knowledge, has so far been made to study $Pb_2Bi_3RTi_5O_{18}$ (R = rare-earth ions) compounds.

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Accordingly, in view of the importance of the materials and non-availability of electrical data, we have carried out to study the structural and electrical properties of $Pb_2Bi_3RTi_5O_{18}$ ceramic prepared by the solid-state reaction method. In the present paper, electrical and dielectric study of $Pb_2Bi_3GdTi_5O_{18}$ ceramic is reported. An attempt has been made to explain the experimental results in the light of their phase transition.

2. Experimental

Polycrystalline $Pb_2Bi_3GdTi_5O_{18}$ (abbreviated as PBGT) was prepared from high purity AR-grade PbO, Bi_2O_3, Gd_2O_3 and TiO by a high temperature solid-state reaction technique. The detailed procedure adopted, for preparation are described elsewhere [21]. The calcination and sintering temperature was 1050°C/10 h and 1100°C/6 h respectively with a heating rate of 4°C/min and the cooling rate of 3°C/min. The completion of the reaction and the formation of the desired compound were checked by X-ray diffraction.

For preliminary structural studies, the X-ray diffractogram of PBGT was recorded at room temperature using CuK_α radiation (λ = 0.15418 nm) over a wide range of Bragg angles ($20° \leq 2\theta \leq 80°$) with a scanning speed of 2° min^{-1}. A sintered pellet was polished and electroded with air-drying silver paste to measure the electrical properties. Electrical impedance (Z), phase angle (θ) and dielectric permittivity were measured as a function of frequency (0.1 kHz-3 MHz) at different temperatures (25–300°C) using HIOKI 3532-50 LCR Hi-Tester, Japan. DC conductivity was measured by using Keithley-617 electrometer. AC conductivity data was obtained from dielectric data, using a relation: $\sigma_{ac} = 2\pi f \varepsilon_0 \varepsilon''$ where f is the operating frequency. ε_0 the vacuum permittivity and ε'' *is* the imaginary part of dielectric constant. To overcome the effect of moisture, if any, on electrical properties, the sample was pre-heated to 150°C and then cooled to room temperature prior to conducting the measurements.

3. Results and discussion

A standard computer program (POWD) has been utilized for the XRD-profile fitting. Good agreement between the observed and calculated inter-planer spacing (d-values) and no trace of any extra peaks, or peaks due to constituent oxides, was found, suggest that the compound is having single phase orthorhombic structure. The lattice parameters were found to be : a = 11.957(7) Å, b = 8.534(9) Å and c = 11.476(8) Å. The estimated error was found to be $\pm 10^{-3}$ Å. The criterion [22] adopted for evaluating the rightness, reliability of the indexing and the structure of PBGT was the sum of differences in observed and calculated d-values $\left(i.e. \sum_{i=1}^{N} |d_{obs} - d_{calc}| \right)$ to be minimum. The unit cell volume ($a \times b \times c$) was calculated to be 1171.29 $Å^3$. The bulk density of the sample was found to be > 90% of the theoretical density.

Figure 1 shows the variation of real (ε') and imaginary (ε'') part of dielectric permittivity, log |Z| and θ with frequency of $Pb_2Bi_3GdTi_5O_{18}$ ceramic at room

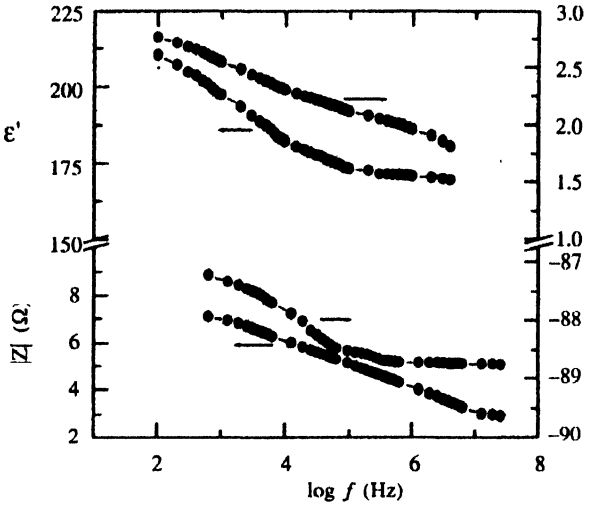

Figure 1. Variation of $\varepsilon', \varepsilon''$, log |Z| and θ with frequency of $Pb_2Bi_3GdTi_5O_{18}$ ceramic at room temperature.

temperature (25°C). All four quantities *i.e.* ε', ε'', log |Z| and θ follow inverse dependence on frequency. This typical behaviour indicates that PBGT behaves like a normal dielectric or ferroelectric materials where different types of polarization mechanisms might be present. We find a similar dielectric behaviour with respect to frequency in other samples of this family *viz.* $Pb_2Bi_3NdTi_5O_{18}$ [21]. The slope of log |Z| *versus* log f gives an idea of phase elements in the circuit [23]. For instance, for merely capacitive element (phase angle 90°), the slope is –1.0 and slope is zero for merely resistive element (no phase change). It can be observed that log |Z| varies linearly with a slope of –0.97 which is close but slightly less than one. Also, the phase angle value lies in the range of –89° to –87° over the investigated frequency range. The room temperature value of $\varepsilon', \varepsilon''$, log |Z| and θ at 1 kHz were found respectively to be 197, 2.549, 6.282 and –87.69°. The low ε'' of this kind can be advantageous when improved detectivity is required.

The temperature dependence of ε' and ε'' of PBGT at 1, 10, 50 100, 500 and 1000 kHz are shown in Figure 2. Both ε'–T as well as ε''–T plots show a broad

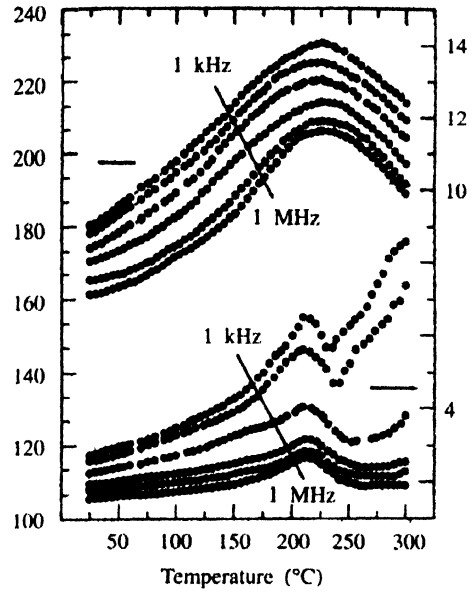

Figure 2. Variation of ε' and ε'' with temperature of $Pb_2Bi_3GdTi_5O_{18}$ ceramic at 1, 10, 50, 100, 500 and 1000 kHz.

maximum at ferro-paraelectric phase transition temperature (T_c) 226°C which clearly indicates the departure from Curie-Weiss law. One can suppose that some disorder in cations distribution (compositional fluctuations) diffuses the phase transition (DPT) where the local curie points of different microregions are statistically distributed around the mean curie temperatures [20]. It has been observed that maximum value of real part of relative permittivity (ε'_{max}) decreases (from 231 at 1 kHz to 206 at 1 MHz) and ε'–T curve flattens with the increase in frequency.

To examine the diffusive character of the ferro-paraelectric phase transition, $1/\varepsilon'-1/\varepsilon'_{max}$ have been plotted against $T-T_c$ in a logarithmic representation (Figure 3). The degree of disorder or diffusivity in PBGT was estimated using least squares fitting (linear) to the expression [24] : $\ln(1/\varepsilon'-1/\varepsilon'_{max}) = \gamma \ln(T-T_c) + a$, where γ is a critical exponent, lies in the range $1 \leq \gamma \leq 2$. $\gamma = 1$ represents ideal Curie-Weiss behaviour while between 1 and 2 indicate diffusive behaviour. The value of γ found to be 1.26.

Figure 4 shows the variation of the imaginary part of impedance, Z'' *versus* real part of impedance, Z' as Cole-Cole plot at 25°C and 300°C. The impedance data do not take the shape of a semicircle rather presents a straight line at room temperature. The large slope (1.31) indicates the insulating behaviour (high resistance) of the sample at room temperature. One high frequency

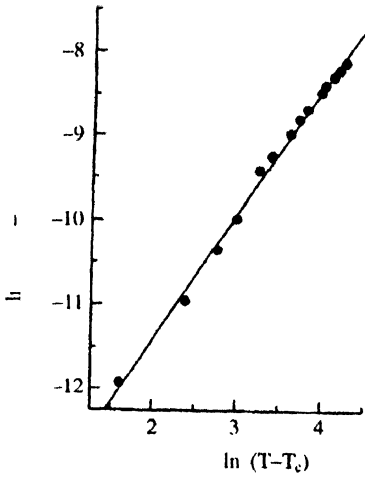

Figure 3. Variation of $\ln(1/\varepsilon'-1/\varepsilon'_{max})$ with $\ln(T-T_c)$ of $Pb_2Bi_3GdTi_5O_{18}$ ceramic at 1 kHz.

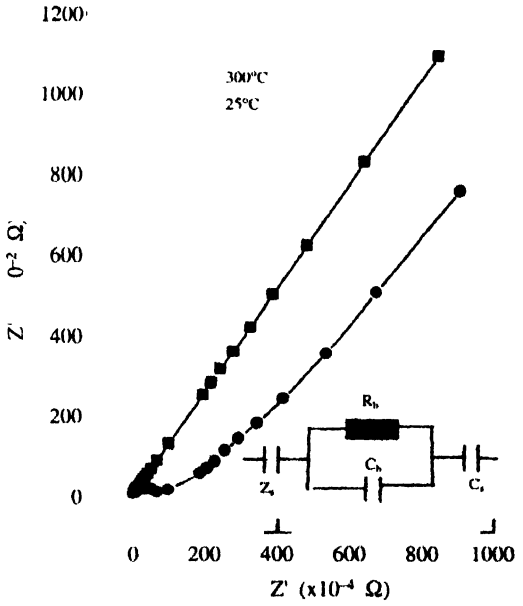

Figure 4. Cole-Cole plot of $Pb_2Bi_3GdTi_5O_{18}$ ceramic.

semicircular arc and a 45° (almost) low frequency straight line have been observed at 300°C. The semicircular arc (representative of grain contribution) starts from 5.7×10^2 kΩ at Z'-axis; hence, there should be a series resistance of the same value that can be ascribed to the LCR circuit representation of the sample [25]. This high frequency semicircle is due to parallel combination of the bulk resistance (R_b) and bulk capacitance (C_b) of PBGT. The capacitance value calculated at the maximum frequency using the relation $2\pi f_{max} R_b C_b = 1$. The characteristic capacitive spike appeared in the plot is

indicative of blocking electrode [25]. A typical representative circuit for the plot at 300°C is shown in Figure 4. The value for R_b and C_b are found respectively to be 680.75 kΩ and 0.39 pF.

Figure 5 shows the variation of $\ln\sigma_{dc}$ against $10^3/T$ at a biasing field of 4.49 kVm^{-1}. The nature of variation is

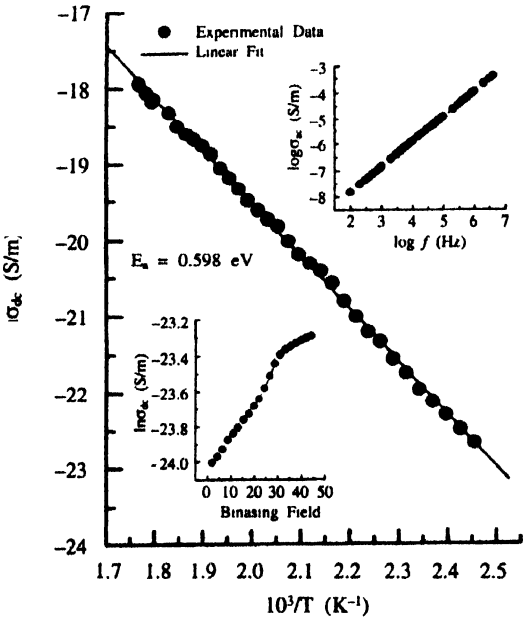

Figure 5. Temperature dependence of dc conductivity of $Pb_2Bi_3GdTi_5O_{18}$ ceramic at constant biasing field 4.49 kV m^{-1}. The inset shows biasing field dependence of the dc electrical conductivity and frequency dependence of ac electrical conductivity at room temperature.

almost linear indicating the ohmic nature of contact and conductivity obeys the Arrhenius relationship : $\sigma_{dc} = \sigma_o \exp(-E_a/kT)$ where E_a is the activation energy of conduction, k is the Boltzmann constant and T is the absolute temperature. The nature of variation shows the negative temperature coefficient of resistance (NTCR) behaviour of PBGT. The value E_a = 0.598 eV obtained by least-squares fitting of the data at higher temperature region. The low value of activation energy obtained could be attributed to the influence of electronic contribution to the conductivity. This value is comparable to other TB-type ferroelectric oxides *e.g.* $Pb_2Bi_3NdTi_5O_{18}$ [21]. We also find that the conductivity inccreases with increasing biasing field at room temperature (inset Figure 5). It can be seen from another inset of Figure 5 that the value of $\log\sigma_{ac}$ (ac conductivity) increases with increase in frequency at room temperature, which is normal trend of a dielectric or ferroelectric. The room temperature value of σ_{ac} at 1kHz was found to be 1.42 × 10^{-7} S/m.

Within the bulk of the material, there are two possible ac conduction mechanisms : (i) the long-range ac conductivity, (ii) local transport of oxygen vacancies. The long-range conduction by vacancies and by the way of charge compensation follows the equation of (Kröger and Vink) : $O_o \rightarrow \frac{1}{2}O_2 \uparrow + V_o^{\bullet\bullet} + 2e^{-1}$ [26]. The oxygen vacancies are created due to the loss of oxygen by $Pb_2Bi_3GdTi_5O_{18}$ during sintering. The value of R^2 (regression coefficient) for all the fittings, quoted in this paper, is excess of 0.999.

4. Conclusion

It is concluded that PBGT has orthorhombic structure at room temperature and undergo diffuse phase transition at 226°C. Also, PBGT has low dielectric constant, low loss and high resistivity. AC impedance analyses suggested the capacitive behaviour of electrode. The nature of variation of resistivity with temperature indicated the negative temperature coefficient of resistivity. The low ε'' of this kind can be advantageous when improved detectivity is required.

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